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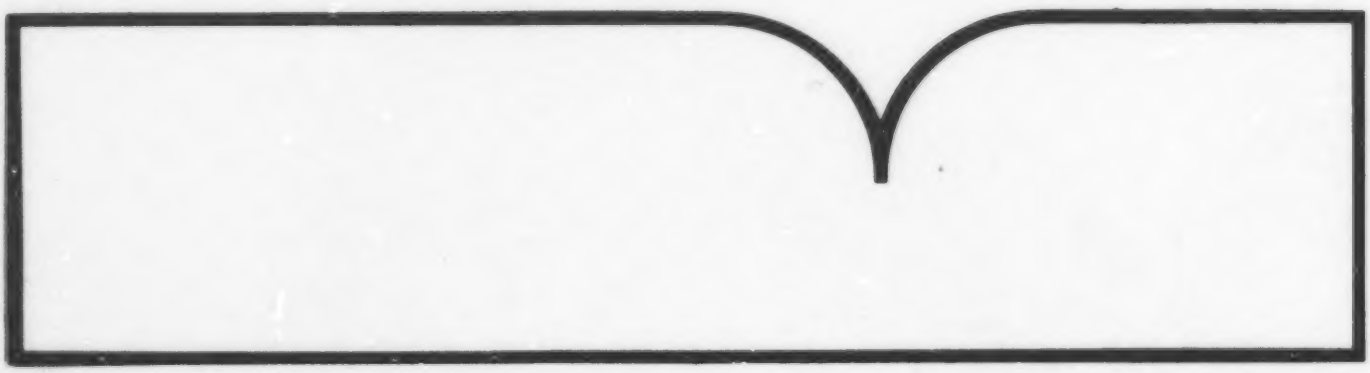

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RECEPTOR MODELING FOR CARBONACEOUS AEROSOLS: SOURCE CHARACTERIZATION

by

S. V. Hering
University of California
Los Angeles, CA 90024

A. H. Miguel
Pontificia Universidade Catolica do Rio de Janeiro, Brazil

R. L. Dod
Lawrence Berkeley Laboratory
Berkeley, CA 94720

J. M. Daisey
New York University Medical Center
New York, NY 10016

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EPA Project Officer
James Cheney

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRAINGLE PARK, NC 27711

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Two types of sources, freeway vehicles and a commercial airport, were sampled with the objective of determining source profiles suitable for receptor modeling of carbonaceous aerosols. A threefold approach is used: 1) measurement of polycyclic aromatic hydrocarbons (PAH) concentrations, 2) bulk characterization of the carbon component by thermal analysis and 3) determination of elemental composition by X-ray fluorescence. Additionally the relative stability of the polycyclic aromatic hydrocarbons upon exposure to filtered urban air was evaluated. Data were collected at a receptor site, which by virtue of its location is expected to be impacted by these two source types.

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RECEPTOR MODELING FOR CARBONACEOUS AEROSOLS: SOURCE CHARACTERIZATION

S.V. Hering, A.H. Miguel[1], R.L. Dod[2], and J.M. Daisey[3]
Department of Chemical Engineering, University of California
Los Angeles, CA 90024

Two types of sources, freeway vehicles and a commercial airport, were sampled with the objective of determining source profiles suitable for receptor modeling of carbonaceous aerosols. A threefold approach is used: 1) measurement of polycyclic aromatic hydrocarbon (PAH) concentrations, 2) bulk characterization of the carbon component by thermal analysis and 3) determination of elemental composition by X-ray fluorescence. Additionally the relative stability of the polycyclic aromatic hydrocarbons upon exposure to filtered urban air was evaluated. Data were collected at a receptor site, which by virtue of its location is expected to be impacted by these two source types.

Sampling Sites and Methods

Vehicular emissions were collected from the airduct of a 1 km freeway tunnel on California State Route 24, east of Berkeley, CA. The individual bores of the tunnel each carried two lanes of unidirectional traffic with a 2^0 grade. Samples were collected for both uphill and downhill traffic for which the traffic mix consisted of less that ½% heavy duty diesels, and for uphill traffic with 2-4% heavy duty diesel trucks. The non-catalyst fraction of the vehicle fleet was estimated by manual counts to be 15-25%. Samples were collected at Los Angeles International Airport 15 meters from the taxiway adjacent to the main runways. The sampling took place in the mornings and evenings under near stagnant conditions with winds less than 5 mph. Samples collected at the airport represent a mix of jet aircraft, prop planes (18% of total aircraft), airport ground vehicles (mostly diesel), and some urban background. Measured soot/Pb ratios at the airport were 12 ± 1 as opposed to 3 ± 1 for the tunnel samples, indicating the dominance of a non-auto combustion source for these airport samples.

Filter samples were collected with three cyclones operated in parallel at a flow rate of 52 lpm to give a precut of 1.3 μm. One of the cyclones used a teflon downstream filter for gravimetric and X-ray fluorescence analyses. The other filters were quartz fiber; one was prefired for thermal analyses, the other unfired for PAH. A HiVolume sampler, employing 20x25 cm quartz filters at $1.4 m^3$/min, was also used for the polycyclic analyses. PAH were analyzed by reverse phase high pressure liquid chromatography with fluorescence or absorbance detection. The carbon thermal analyses were performed by heating the sample in an oxidizing atmosphere, and measuring the CO_2 evolved. Simultaneous measurement of the filter opacity during combustion allows the high temperature (~500^0 C) peak to be identified as "black" (presumably soot) carbon. (Ellis and Novakov, 1983)

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1 Pontificia Universidade Catolica do Rio de Janeiro, Brazil
2 Lawrence Berkeley Laboratory, Berkeley, CA 94720
3 New York University Medical Center, New York, NY 10016

Carbon Thermal Analyses (Thermograms)

The data collected here can be catogorized into 5 classes: (1) uphill freeway traffic with 2-4% heavy duty diesel (HDD), (2) uphill freeway traffic of 0-½% HDD, (3) downhill traffic with 0-½% HDD, (4) airport sampling and (5) receptor site sampling. Thermograms from each of these five classes are shown in Figure 1. Although not shown here, these thermal profiles are quite consistent within a specified source type. There is no significant difference between the uphill freeway samples with 2-4% truck diesels as opposed to those with 0-½% truck diesels. For the downhill traffic, the percentage of carbon associated with the 500°C "black carbon" peak is smaller. The airport thermogram has a more rounded black carbon peak as does that of the receptor site.

Although the thermograms offer encouragingly different signals for the tunnel and airport sources, there are several questions which must yet be addressed. First, the stability of the thermograms with respect to atmospheric reactions should be established. For source resolution one must know how similar the thermograms measured at the source are to the aged source aerosol seen at the receptor site. Secondly, one must show whether the principle of linear superposition, tacitly assumed in all receptor modeling, is valid for the thermograms.

Polycyclic Aromatic Hydrocarbon Profiles

One method of presenting PAH profiles would be to divide the concentration of each compound by the total fine mass loadings. This would be analogous to the elemental profiles developed for elemental mass balance analysis. The difficulty is these compounds ~~are~~ known to react in a polluted atmosphere (eg. Grosjean et al, 1983). Thus, the mass fraction of a primary polycyclic hydrocarbon observed in the aged aerosol of the receptor site will not be the same as at the source. Lifetime studies conducted by A. Miguel (1984) on our Caldecott freeway tunnel samples showed 35-100% PAH losses upon 4 day exposure to filtered Los Angeles air. However, five of the compounds chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, indenopyrene and benzo(ghi)perylene where found to decay at a similar rate, so that the percentage of a specified PAH of the total PAH considered is relatively constant (Figure 2).

PAH profiles expressed as a fraction of the sum of PAH loadings ($PAH_i / \Sigma_i\ PAH_i$) are shown in Figure 3 for our five data types. Unfortunately we do not see any marked differences here. The profiles of the different source types, and of the receptor site are quite similar. We note that these four PAH compounds have previously been identified in the exhausts of aircraft turbines (Spitzer and Dannecker, 1983) and automobiles (National Research Council, 1983).

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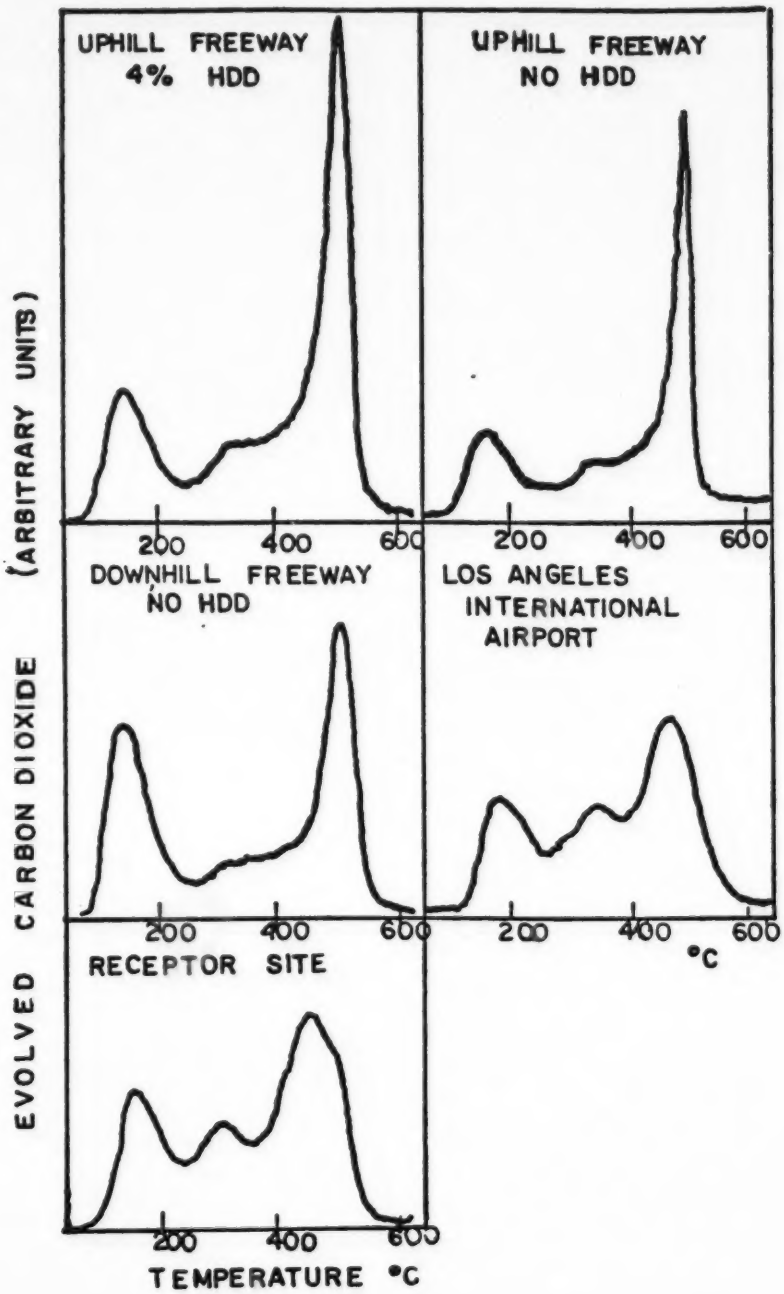

Figure 1. Relative CO_2 evalued as a function of temperature for five samples corresponding to (1) uphill freeway traffic with 4% HDD, (2) uphill freeway no HDD, (3) downhill freeway no HDD, (4) LA International Airport, (5) receptor site near freeway and airport.

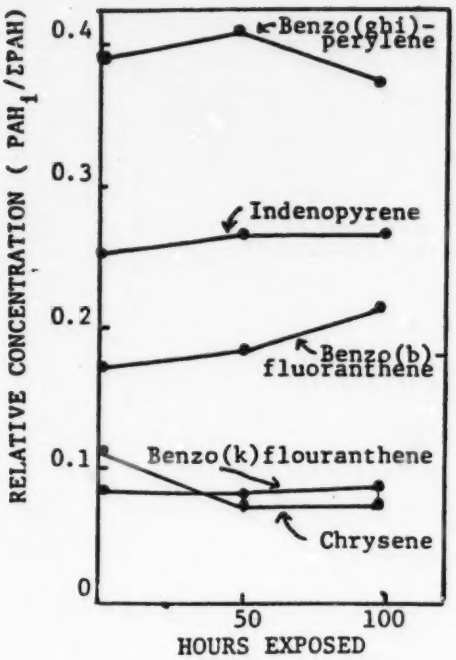

Figure 2. Relative concentrations of PAHs collected in a freeway tunnel and exposed to filtered Los Angeles air (data from Miguel, 1984).

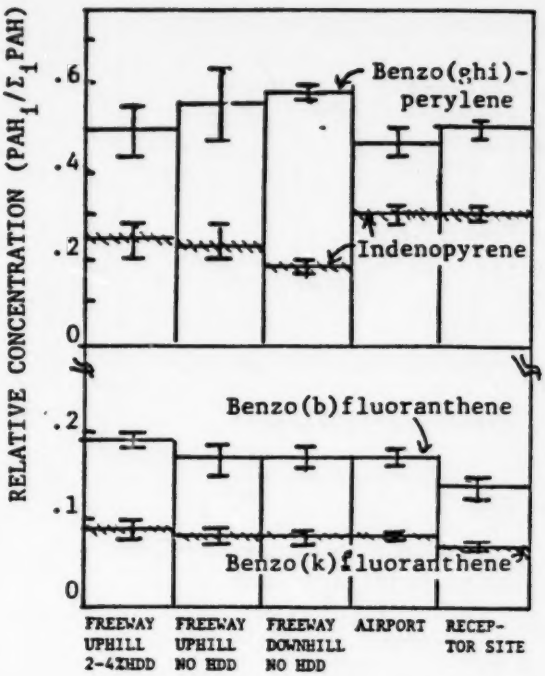

Figure 3. Average relative concentration of some PAHs for four types of source samples and one receptor site. Error bars represent standard deviations among successive measurements.

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